ndian J. Phys. 76A (1), 15-17 (2002)

IJP A

— an international journal

Refractive index measurement as a function of temperature of the mesogen trans, trans-4'-propyl-bicyclohexyl-4-carbonitrite

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bstract The mesogen $CCH_3(C_{16}H_{27}N)$ is a member of the homologous series of trans, trans-4'-propyl-bicyclohexyl-4-carbonitrite (cy-ohexylcyclohexanes or CCH's) having the structural formula C_nH_{2n+1}-⟨H⟩-⟨H⟩- CN, $n = 3$ for CCH_3.

Though much work has been done on different members of the series, the orientational order parameter $<P_2>$ as a function of temperature has not en reported so far for CCH_3. With a view to determine the variation of $<P_2>$ with temperature and to study the effect of increasing chain length on e optical properties of this homologous series, an indigenous experiment for birefringence studies at different temperatures using a laser beam has en set up. Ordinary and extraordinary refractive indices (n_o, n_e) have been determined as a function of temperature. From these values and from ensity measurements, polarisabilities α_0 and α_e and hence $<P_2>$ may be determined

eywords Mesogen, thermotropic, birefringence, order parameter

ACS Nos. : 61 30 -v, 78 20 Fm, 78.20 Ci

. Introduction

Much work has been done on the series trans, trans-4'-alkyl-icyclohexyl-4-carbonitriles (abbreviated to cyano cyclohexyl yclohexanes or CCH) and having the structural formula C_nH_{2n+1}-⟨H⟩-⟨H⟩- CN.

Following their synthesis [1], dielectric and optical nisotropy measurements have been conducted [2] on some members of the CCH's. X-ray crystal structure of some members namely CCH_3, CCH_5 and CCH_7 in the solid phase have been letermined [3] and diffraction work conducted on some members 4, 5]. Elastic constants of CCH_3 and CCH_5 have been letermined[6] and IR/Raman scattering studies have been onducted on some members of the series [7]. The variation of order parameter with temperature from birefringence studies have not been reported so far.

With a view to studying the optical anisotropy at different emperatures of the mesogens an indigenous experiment has een set up based on the principle of Chatelaine Wedge [8] nethod, using a laser beam. Birefringence studies have een conducted on a particular member CCH_3 at various emperatures.

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2. Experimental observations

A. Texture studies :

The sample CCH_3 undergoes the following transitions (supplied by Merck Ltd.)

$$\text{solid} \xrightarrow{58^\circ c} \text{nematic} \xrightarrow{80^\circ c} \text{isotropic}$$

$$\downarrow 57^\circ c$$

$$\text{smectic} \xleftarrow[44^\circ c]{} \text{smectic} \xleftarrow[48^\circ c]{} \text{smectic}$$

Microscopic studies have confirmed the validity of the above temperatures. The nature of the changes at different temperatures was examined and transition temperatures noted using a polarising microscope (Leitz) having a hot stage (Mettler F82HT). Observation was performed on the sample under crossed polarisers with a magnification of 150X. However, no observations could be made below 30°C due to technical difficulties. Heating and cooling were done at the rate of 1°C/ min. The sample was heated to temperatures well above the isotropic transition temperatures and then allowed to cool. The sample on heating melts at 58°C to nematic phase. At 80°C, it passes to the isotropic phase. On cooling, it passes to the smectic *B* phase at 57°C. Subsequently at 48°C and 44°C, it undergoes phase transition to other smectic phases which have not been identified so far.

B. *Refractive index measurements*

We have conducted refractive index measurements at different temperatures covering the entire nematic phase by Chatelaine Wedge method using a laser beam. The details of the experimental arrangement, which has been designed, fabricated and set-up, is given below.

Experimental arrangement :

A brass sample holder (Figure 1) with an electrical heating arrangement, such that the sample may be heated at any temperature upto 200°C has been fabricated in house. The heating wire is Kanthal (~ 40W resistance) and is wound in a

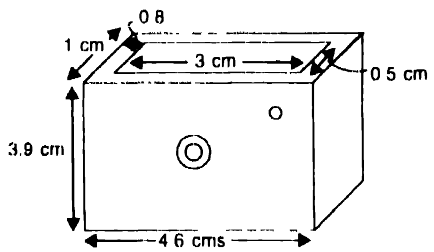

Figure 1. Sample holder

noninductive winding around the sample holder so as to not to obstruct the path of the incoming and outgoing beam. A hole drilled in the sample holder allows the light to be made incident on the sample normally. A diverging hole drilled coaxially allows the refracted beam to pass unhindered so as to fall on a screen held several meters away The temperature of the sample holder and therefore the sample was regulated by means of a temperature controller whose thermocouple probe was inserted in a hole drilled in the sample holder To ensure that there is no heat loss through dissipation, the brass block is thickly coated with cement.

Sample preparation .

Glass slides cut to the required size were surface–treated with polyvinyl alcohol. On evaporation, polyvinyl alcohol leaves a thin coating on the glass surface, which on rubbing along a direction parallel to the edge of the slide (edge of the prism to be formed), produces parallel etchings. Hollow prisms were formed by gluing the edges, the untreated surfaces being kept outwards. This surface treatment ensures better alignment of the sample to be introduced.

Prior to introduction of the sample, the prism angle was determined. This was done by directing a laser beam on the prism at near normal incidence and measuring the positions of the two spots obtained by reflection from the front and back surfaces of the prism on a screen kept 350 cms away. The vertical separations of the spots were ~ 20 cms. The vertical and horizontal distances of the spots from the prism enable the prism angle to be determined. The spots are rather sharp and spot size negligible. Prisms of angles 1° – 2° were used. The liquid crystal sample was introduced through the top of the wedge (which was kept open) by melting the liquid crystal and allowing the melted sample to flow in. The open edge was then sealed. The sample cell (prism) was then encapsulated in the sample holder.

Experimental procedure :

The sample encapsulated in the sample holder was placed in an aligning magnetic field of 8 kGauss, the direction of the field being parallel to the direction of rubbing of the internal surfaces of the prism. The sample was subjected to repeated temperature cycling from the room temperature to well above the N-I transition temperature, in the presence of the magnetic field. The combination of rubbing and repeated temperature cycling in the magnetic field produces a homogeneous nematic specimen with the optic axis parallel to the edge of the prism. Light from a He-Ne laser (λ = 633 nm) was made incident on the sample normally through the hole drilled in the sample holder. The angular deflections of the refracted beams were measured by observing the positions of the light spots on a screen held ~ 4 mts (395 cms) away. From the changes in the patterns observed on the screen, the transition temperature may be verified. They were found to be in conformity with the temperatures obtained from texture studies. The sample was heated at the rate of 1°C / min to temperatures beyond the isotropic temperature and allowed to cool at the same average rate. The vertical heights of the spots due to E and O rays above the direct beam (BE and BO, Figure 2) and the screen to prism distance (AB, Figure 2) enable the refractive indices n_e and n_o to be determined using

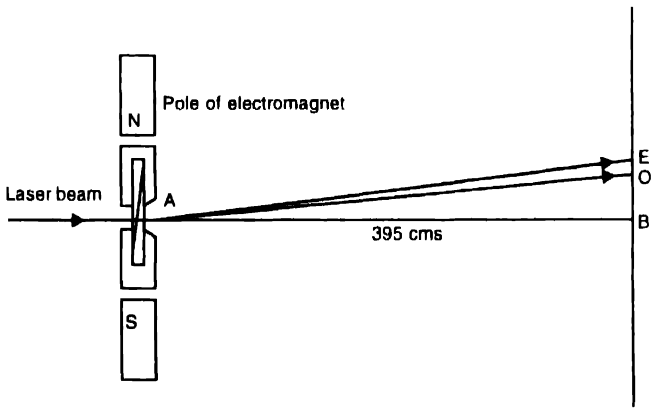

Figure 2. Schematic diagram of the experimental set-up

the prism angle. These spots formed by the beams passing through the liquid crystal sample have a width of ~ 0.5 cms. The spot separation varies but is typically of ~ 1 cms. Thus for measurements of vertical heights, the heights of top and bottom ends of each of the circular spots were taken and the mean of these values used to give the vertical heights. The angular deflections were thereupon determined and the refractive indices n_e and n_o were calculated at different temperatures over the temperature range of 57°C to 78°C (the nematic range).

Results and discussion

'able 1 lists the values of n_e , n_o and anisotropy $\Delta n = n_e - n_o$ s a function of temperature. We find that the anisotropy values

'able 1. Variation of refractive indices (n_o, n_e) with temperature of CCH_3

Temp (°C)	n_o	n_e	Δn
59	1.543	1.601	0.058
61	1.543	1 601	0 058
63	1 547	1.597	0.050
65	1 547	1 597	0 050
67	1 547	1.597	0.050
69	1.551	1 593	0 042
71	1.551	1 593	0 042
73	1.551	1 588	0.037
75	1.556	1 588	0 032
77	1 556	1 580	0 024
79	1 560	1 560	0.000

of 0.06 quoted at 20°C agrees well with the order of anisotropy obtained by us. The anisotropy falls gradually and finally vanishes at t_{NI} (nematic-isotropic transition temperature) as expected. Comparing these n_o , n_e values with those of CCH_4 and CCH_5 obtained by us [10] and elucidated in Figure 3 we find that the values of CCH_4 are lower than those of CCH_3 and CCH_5. Bradshaw and Raynes [6] have reported $\bar{\varepsilon}$ as a function of temperature for the odd members of the homologous series

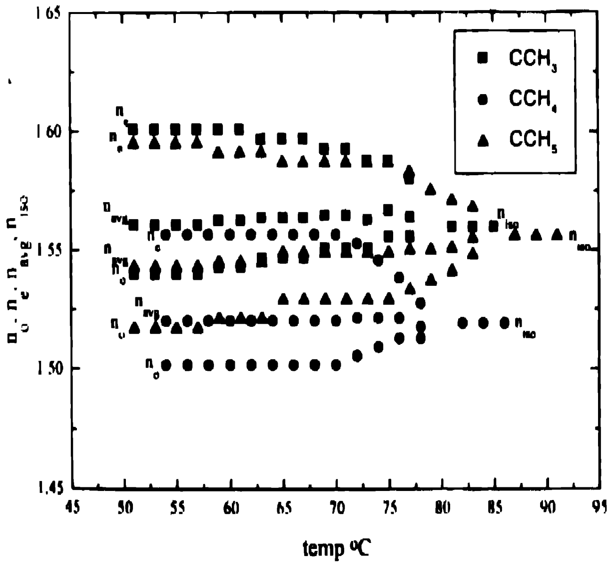

Figure 3. Variation of n_o, n_e with temperature of CCH_n, n = 3,4,5 and $\bar{n}^2 = (n_e^2 + 2n_0^2)/3$.

CCH_3, CCH_5 and CCH_7. With increasing chain length, both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ decrease.

4. Conclusion

We find that n_0 and n_e decrease for higher members of the homologous series *i.e.*, there is a decrease of refractive index with increasing chain length for odd members. If the densities of the sample are determined at various temperatures, then the principal molecular polarisabilities (α_0, α_e) may be calculated using Vuks' [9] or Neugebauer's formula [11]. The order parameters may be determined as a function of temperature using the relation

$$< P_2 >=(\alpha_e - \alpha_o)/(\alpha_{\parallel} - \alpha_{\perp}). \quad (1)$$

Determination of density, calculation of polarisabilities α_0, α_e and hence $<P_2>$ as a function of temperature are now in progress.

Acknowledgments

We are thankful to Merck Ltd. for supplying the samples. We are grateful to Prof. R Paul and Dr. S. Paul of Department of Physics, North Bengal University for their valuable suggestions. Thanks are due to Dr. C. D Mukherjee of Saha Institute of Nuclear Physics. Thanks are due to Prof. P. Nandy and Dr. R. Basu of department of Physics, Jadavpur University for helping us with the texture studies.

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